



Modeling of the catalytic removal of CO and NO under lean-burn conditions: Can there be too much catalyst?

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ABSTRACT

The NO + CO + O₂ reaction under net-oxidizing conditions may demonstrate an interesting phenomenon: the conversion of NO to N₂ decreases when the amount of catalyst increases. This behavior has been observed in many experimental studies and, as a rule, it has been attributed to the structural sensitivity of the catalytic reaction. Using the classical theories of heterogeneous catalytic reactions and chemical reactors, we demonstrate that this unusual effect can be well explained by the peculiarities of the reaction mechanism and kinetics of competing reactions.

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1. Introduction

Considerable improvement in fuel economy can be achieved for lean-burn gasoline and diesel engines. These devices yield a more complete combustion and reduce the fuel consumption compared to stoichiometric combustion thus reducing the amounts of CO₂, CO and hydrocarbons emitted during driving. Unfortunately, the nitrogen oxides NO_x ($x = 1, 2$) are produced too, but the conventional three-way catalyst is ineffective for NO_x reduction because of oxygen-rich conditions. During the past two decades, the catalytic removal of nitrogen oxides in the presence of excess oxygen was one of the most important targets in environmental catalysis research. In addition to CO and hydrocarbons, hydrogen and ammonia have been proved to act as effective reductant for NO removal under lean-burn conditions. Various technologies such as NO_x storage-reduction (NSR) [1] and selective catalytic reduction (SCR) [2] have been developed. The first NSR catalyst was created and put into the market by Toyota in 1994. NSR combines storage of NO_x in the catalytic converter with mixed lean-rich operation of the engine. SCR of NO_x by hydrocarbons has been extensively investigated since early 1990s and hundreds of catalysts have been

evaluated. However, these technologies are still under development. In the last years, research has focused on expanding the operability and durability as well as on reducing the cost and complexity of both SCR and NSR.

The unusual behaviors during the removal of NO under strongly oxidizing conditions were described in 1970s at the early stages of research regarding the three-way catalyst. For example, Schlatter and Taylor [3] discovered that after the thermal aging of Rh/Al₂O₃ catalyst, the NO conversion efficiency was improved under the lean-burn conditions. They had also mentioned the following: “Surprisingly, a 50-fold decrease in Rh loading showed little effect on NO removal efficiency and NH₃ formation”. Tauster and Murrell [4] studied the NO + CO reaction in the presence of excess O₂ using 0.001% Ir/Al₂O₃ and 0.1% Ir/Al₂O₃ catalysts. They discovered that a catalyst with low Ir content achieved slightly higher degree of NO reduction, as compared to a catalyst which contains 100 times more iridium. This “surprising” result was tentatively ascribed to a difference in iridium crystallite size between the two catalysts. Taylor and Schlatter [5] studied the NO + CO reaction on Pt, Ir, Rh and Pd. They wrote: “the 0.002 wt% Pt/Al₂O₃ catalyst was more selective for NO conversion than the 0.06 wt% Pt/Al₂O₃ catalyst (Fig. 6)”. This figure shows that at 550 °C the catalyst with low Pt content was 2–3 times more active regarding NO reduction than the catalyst with high Pt content. Similar results were obtained for Ir and Rh. Iridium was found to be the most active metal to catalyze the NO + CO + O₂ reaction.

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During the next thirty years of research, numerous studies, which used different precious metals and reducing reagents, had shown that under the lean-burn conditions at some temperature, the rate of NO conversion was improved when decreasing the amount of catalyst. The variation of the active catalytic surface area was achieved due to metal loading, metallic dispersion, or thermal aging of catalyst. For example, the results presented by Burch et al. (see Fig. 2 in [6]) clearly showed that at elevated temperature the decrease of Pt content resulted in the increase of NO conversion. The more recent work [7] gives the rate of NO reduction per unit mole of Ir for Ir/WO₃ catalysts with different metal loadings (Fig. 2 in Ref. [7]). The rate of NO conversion shows a maximum at a small Ir loading of 0.5–1.0 wt%. If the metal loading is 10 times higher, then the rate of NO reduction per unit mole of Ir decreases about 10 times. Once again, these unusual results, which already became typical for experimental studies of NO removal under the lean-burn conditions, were attributed to a structural sensitivity of the reaction. In addition, it was discovered that Ir/WO₃ and Ir/SiO₂ are active for NO reduction with CO in the presence of both O₂ and SO₂ [8,9]. The paradoxical feature of this reaction is that the presence of SO₂, which normally poisons the active sites and significantly decreases the catalytic activity, actually promotes NO reduction in the presence of O₂.

While fundamental studies have revealed a number of important features of the surface chemistry, the elementary mechanism for NO_x reduction under oxidizing conditions is still not well understood. Logic and intuition tells us that a decrease in the active catalyst surface area should result in a comparable reduction in the reaction yield and efficiency. Only when there is a complete conversion of all reagents and efficiency is close to 100%, then one can expect that a decrease in the catalyst surface area may have a little influence on the results. For most catalyzed reactions, the more catalyst used, the faster is the reaction. These expectations are reasonable if there is a single reaction product. With a complex reaction network and several competing reactions, the results are not so evident. Nevertheless, if an increase in the catalyst loading would suddenly give a decrease of the reaction rate(s), an experimentalist (after careful check of the results) would probably decide that added catalyst also resulted in some structural changes of the catalyst particles. These changes, in turn, somehow worsen the total catalytic activity.

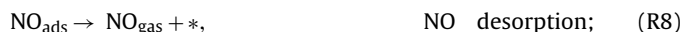
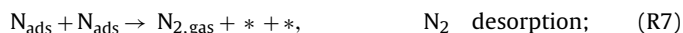
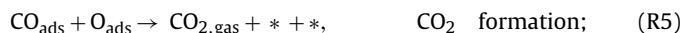
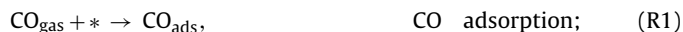
In summary, there are many experimental results showing the unusual phenomena during the removal of NO under strongly oxidizing conditions. In general, the surprising results were tentatively attributed to “structural sensitivity” of the NO decomposition reaction. Are there any other reasonable explanations of why this may happen? Our theoretical study just gives the alternative explanation which is based on the peculiarities of the reaction mechanism and the steady-state kinetics of competing reactions. We applied only the classical theories of heterogeneous chemical reactions such as the law of mass action, the transition-state theory, the theory of ideal gas, and assumptions of isothermal continuous-stirred-tank reactor (CSTR).

2. Reaction mechanism and mathematical model

2.1. Kinetic scheme

The phenomenon we would like to describe was originally discovered in a complex model of catalytic monolith reactor. To elucidate the origin of the unusual behavior, we simplified the reaction mechanism as much as possible, and also we assumed the isothermal CSTR model. To model the simultaneous catalytic removal of

NO and CO under the lean-burn conditions, we use the following elementary steps:



Here, the asterisk (*) denotes an empty adsorption site on the catalyst surface; subscripts “gas” and “ads” indicate species in the gas phase and in the adsorbed layer, respectively. The molecules of CO₂, N₂, and O₂, which are produced via the steps (R5), (R7) and (R10), are assumed to desorb from the surface immediately after the formation reaction. For simplicity, the other possible reaction products, such as N₂O and NO₂, are not considered.

2.2. Rate constants

The rate constants for the adsorption steps, k_i ($i = 1-3$), had been estimated using the kinetic theory of gases:

$$k_i = \frac{s_i^0}{(2\pi m_i k_B T_{\text{gas}})^{1/2} N_s},$$

where s_i^0 is the initial sticking coefficient; m_i is the molecular mass [kg]; k_B [J/K] is the Boltzmann constant; T_{gas} [K] is the gas temperature; N_s is the number of surface sites per unit area. We adopted the following values: $N_s = 10^{19} \text{ m}^{-2}$, $T_{\text{gas}} = 300 \text{ K}$, $s_1^0 = s_2^0 = s_3^0 = 0.1$. The rate constants, in the units [$\text{s}^{-1} \text{ Pa}^{-1}$], are approximately as follows:

$$k_1 \approx 287.48, \quad k_2 \approx 268.91, \quad k_3 \approx 277.73.$$

The rate constants, k_i [s^{-1}] ($i = 4, \dots, 10$), for the steps (R4)–(R10) are calculated using the Arrhenius formula:

$$k_i = k_{0,i} \exp\left(-\frac{E_i}{RT_{\text{cat}}}\right),$$

where $k_{0,i}$ [s^{-1}] is the prefactor; E_i [kJ/mol] is the activation energy; R [kJ/(mol K)] is the ideal gas constant; T_{cat} [K] is the catalyst temperature. In our study we used “typical” values of prefactors and activation energies. The adopted values are collected in Table 1.

Table 1
Rate constants.

Step, i	$k_{0,i}$ [s^{-1}]	E_i [kJ/mol]
4. CO desorption	10^{15}	135
5. CO ₂ formation	10^{13}	90
6. NO dissociation	10^{13}	90
7. N ₂ desorption	10^{12}	90
8. NO desorption	10^{15}	130
9. NO formation	10^{13}	130
10. O ₂ desorption	10^{13}	220

2.3. Evolution equations for surface coverage and partial pressures

To write out the equations of the isothermal CSTR model, we use the following notations. Let P_{CO} , P_{O_2} , P_{NO} are the partial pressures of CO, O₂, NO, respectively, in the gas mixture inside the reactor. The surface coverage of adsorbed species are denoted as θ_{CO} , θ_{O} , θ_{NO} , θ_{N} . The surface coverage of empty sites, θ_* , is calculated as $\theta_* = 1 - (\theta_{\text{CO}} + \theta_{\text{O}} + \theta_{\text{NO}} + \theta_{\text{N}})$.

The rates of elementary steps, r_i , are calculated in the framework of the mass action law. It is assumed that the adsorbed layer is randomly well-mixed, and lateral interactions are neglected. According to the kinetic scheme (R1)–(R10), the individual rates are calculated as follows:

$$r_1 = k_1 P_{\text{CO}} \theta_*,$$

$$r_2 = k_2 P_{\text{O}_2} \theta_*^2,$$

$$r_3 = k_3 P_{\text{NO}} \theta_*,$$

$$r_4 = k_4 \theta_{\text{CO}},$$

$$r_5 = k_5 \theta_{\text{CO}} \theta_{\text{O}},$$

$$r_6 = k_6 \theta_{\text{NO}} \theta_*,$$

$$r_7 = k_7 \theta_{\text{N}}^2,$$

$$r_8 = k_8 \theta_{\text{NO}},$$

$$r_9 = k_9 \theta_{\text{O}} \theta_{\text{N}},$$

$$r_{10} = k_{10} \theta_{\text{O}}^2,$$

The evolution equations for the surface coverage reflect the mass balance on the catalyst surface. They are as follows:

$$\dot{\theta}_{\text{CO}} = r_1 - r_4 - r_5,$$

$$\dot{\theta}_{\text{O}} = 2r_2 - r_5 + r_6 - r_9 - 2r_{10},$$

$$\dot{\theta}_{\text{NO}} = r_3 - r_6 - r_8 + r_9, \quad (1)$$

$$\dot{\theta}_{\text{N}} = r_6 - 2r_7 - r_9,$$

where the dot indicates the time derivative.

The CSTR model is characterized by the following parameters: the reactor volume V [m³]; the flow rate of gas mixture F [m³/s] (pumping speed); the inlet partial pressures $P_{\text{CO}}^{\text{in}}$, $P_{\text{O}_2}^{\text{in}}$, and $P_{\text{NO}}^{\text{in}}$ [Pa]. The equations governing evolution of the partial pressures of reactants inside the reactor can be obtained assuming ideal gas behavior. They are as follows:

$$\begin{aligned} \dot{P}_{\text{CO}} &= \frac{(P_{\text{CO}}^{\text{in}} - P_{\text{CO}})}{\tau} - \sigma(r_1 - r_4), \\ \dot{P}_{\text{O}_2} &= \frac{(P_{\text{O}_2}^{\text{in}} - P_{\text{O}_2})}{\tau} - \sigma(r_2 - r_{10}), \\ \dot{P}_{\text{NO}} &= \frac{(P_{\text{NO}}^{\text{in}} - P_{\text{NO}})}{\tau} - \sigma(r_3 - r_8). \end{aligned} \quad (2)$$

The first term in the right-hand side of each equation is the rate of partial pressure changes due to gas flow; $\tau = V/F$ [s] is the residence time of the reactor. The second term accounts for a change of partial pressure due to mass exchange between the gas phase and the catalyst surface via adsorption and desorption. The coefficient

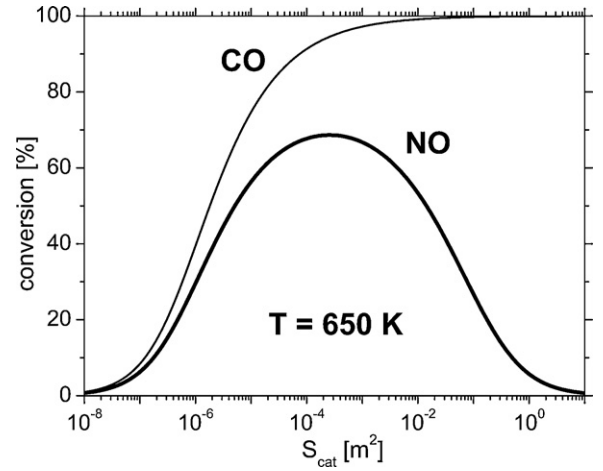


Fig. 1. Steady-state conversions of NO and CO as a function of the catalyst surface area at $T = 650$ K.

$\sigma = N_s k_B T_{\text{gas}} S_{\text{cat}} / V$ [Pa], where S_{cat} [m²] is the catalyst surface area, is calculated from the ideal gas equation of state.

We are interested only in the steady states solutions of Eqs. (1) and (2). Note that under the steady-state conditions, the solution is independent on the value of V . For the calculations presented in this study, we used the following fixed values of parameters: $N_s = 10^{19}$ m⁻², $T_{\text{gas}} = 300$ K, $F = 2 \times 10^{-6}$ m³/s; $P_{\text{CO}}^{\text{in}} = 7.5 \times 10^2$ Pa, $P_{\text{O}_2}^{\text{in}} = 2 \times 10^3$ Pa, $P_{\text{NO}}^{\text{in}} = 10^2$ Pa. The catalyst surface area S_{cat} and its temperature $T = T_{\text{cat}}$ are varied.

3. Results and discussion

To calculate the steady-state solutions of Eqs. (1) and (2), we apply pseudo-arclength continuation with S_{cat} or T as a bifurcation parameter. Figs. 1 and 2 demonstrate the steady-states as a function of S_{cat} at fixed $T = 650$ K. The NO and CO conversions are shown in Fig. 1. Fig. 2 illustrates the partial pressures [frame (a)], the adsorbate coverages [frames (b), (c), (d)], and the total rates of some reactions [frames (e), (f)]. The total reaction rates are defined as $r_i^{\text{tot}} = r_i S_{\text{cat}}$.

In Fig. 1 one can see the interesting effect: the NO conversion decreases when the catalyst surface area increases. The maximum of NO conversion, about 69%, is achieved for $S_{\text{cat}}^* \approx 2.61 \times 10^{-4}$ m². However, when $S_{\text{cat}} = 10$ m², the conversion of NO is less than 1%. At the same time, conversion of CO to CO₂ always grows as the catalyst surface area increases. Non-monotonic dependence of the NO conversion on the catalyst surface area is explained by the following items:

- (1) NO dissociation is the reversible reaction.
- (2) NO dissociation requires an adjacent vacant site, so that on a largely occupied surface this reaction is inhibited.
- (3) The conversion of NO to N₂ occurs simultaneously with the CO oxidation reaction; the reactants in each reaction compete for the same catalytic sites.
- (4) When the catalyst surface area is large, CO is largely converted into CO₂, the partial pressure and surface coverage of CO drop to almost zero, and the surface becomes occupied by atomic oxygen because O₂ is in excess.
- (5) The surface coverage by atomic oxygen grows as the catalyst surface area increases.
- (6) When the catalyst surface is largely occupied by atomic oxygen, the rates of NO dissociation and NO formation become close to each other, as a result, the conversion of NO to N₂ is very low.

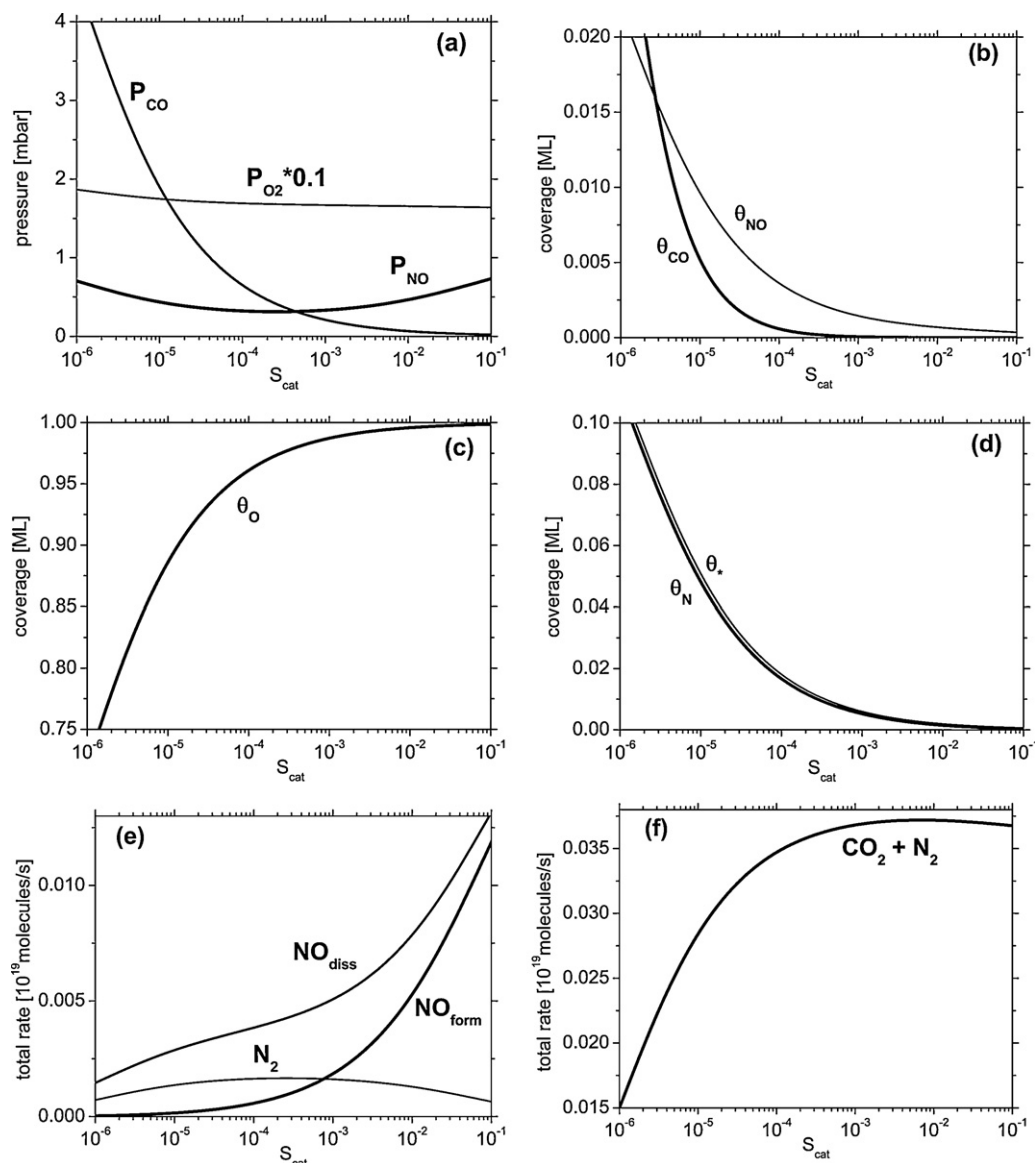


Fig. 2. The solutions for the data presented in Fig. 1. (a) Partial pressures P_{CO} , P_{O_2} and P_{NO} ; (b) adsorbed CO and NO coverage; (c) atomic oxygen coverage; (d) atomic nitrogen coverage and concentration of vacant sites; (e) total rates of NO dissociation, NO formation and N_2 formation (f) sum of the total rates of CO_2 and N_2 formation.

In summary, when S_{cat} is increased, the CO conversion and the surface oxygen coverage increase too. High oxygen coverage, in turn, promotes the rate of NO formation and inhibits NO dissociation, and as a result, the NO conversion can decrease.

Fig. 2(e) shows the total rates of the NO dissociation and formation reactions. The plot (not shown) of $(r_6^{\text{tot}} - r_9^{\text{tot}})$ versus S_{cat} is qualitatively the same as for the NO conversion shown in Fig. 1. At high values of S_{cat} , the rates of NO formation and NO dissociation become almost equal. This happens despite the fact that the activation energy of NO dissociation is lower than the activation energy of NO formation by 40 kJ/mol, so that the rate constants of NO dissociation and NO formation differ by a factor of ~ 160 at $T = 650$ K. The concentrations of the atomic nitrogen and empty sites are almost identical (Fig. 2(d)). However, the coverage of atomic oxygen (Fig. 2(c)), which is required for NO formation, significantly exceeds the coverage of NO (Fig. 2(b)), which is required for NO dissociation. It is the high oxygen coverage that explains the low NO conversion at high values of S_{cat} . It should be stressed that the increase of NO conversion upon decrease of S_{cat} can only be observed if oxygen is in the large excess.

Remarkably, the sum of the total rates of CO_2 and N_2 formation (see Fig. 2(f)) gives a very weakly defined maximum for $S_{\text{cat}} \approx 0.008 \text{ m}^2$. These two species are the only reaction products; therefore, the total catalytic activity also exhibits non-monotonic dependence on S_{cat} , but this effect is not pronounced. Such behavior is probably impossible as long as there is a single reaction product. Nevertheless, the amount of catalyst's surface area can really be "too much" for a complex catalytic reaction with several products.

The results similar to that presented in Figs. 1 and 2, can also be obtained for other values of the flow rate F , since the stationary solutions depend on a ratio F/S_{cat} only. In particular, for any finite value of F , there is a value of S_{cat}^* for which the NO conversion is maximum. We fixed the flow rate at $F = 2 \times 10^{-6} \text{ m}^3/\text{s} = 120 \text{ cm}^3/\text{min}$ in order to match the typical laboratory experiments.

The relevance of reaction (R9) for the theoretical description of the NO decomposition on Pt had been discussed in [10]. Usually, this reaction is neglected in the models concerning the three-way catalytic converters (as an exception, see e.g. [11]), but it is included in the reaction mechanism when the ammonia oxidation reaction is

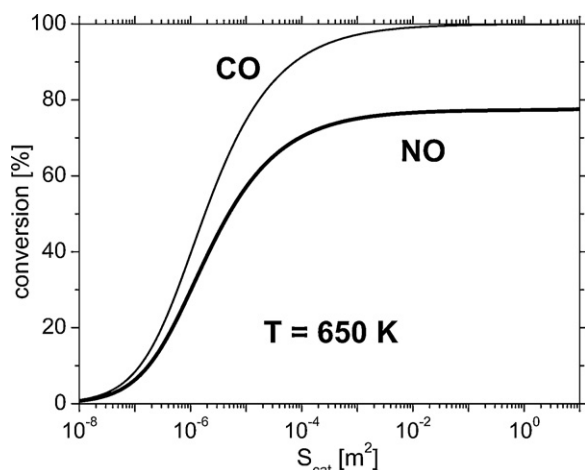


Fig. 3. Steady-state conversions of NO and CO as a function of the catalyst surface area at $T = 650$ K, when the reaction of NO formation is removed from the reaction mechanism.

considered (e.g. [12]). The reaction of NO formation can explain the volcano-shaped dependence of the NO conversion on temperature under the lean-burn conditions. The gradual decrease of the NO conversion with increasing temperature is caused by the growing rate of this reaction. It also plays a key role in the non-monotonic dependence of the NO conversion on S_{cat} , as discussed above. Fig. 3 demonstrates what happens with the NO and CO conversions when the reaction (R9) is removed from the reaction mechanism ($k_9 = 0$). As expected, in this case both the NO and CO conversions are monotonically increasing when S_{cat} grows.

Fig. 4 demonstrates the steady-state NO and CO conversions and the surface coverages as a function of catalyst temperature

at a fixed value $S_{cat} = 0.01$ m². In the temperature range of about 450–550 K, there are three steady-states, two of which are stable. Solid lines denote stable solutions while dashed lines denote the unstable ones. At low (high) temperatures, the catalyst's surface is predominantly covered by adsorbed CO (O) while the O (CO) coverage is low. The adsorbed NO and N are present in essential amounts only in the region of bistability. In Fig. 4(d) for the variables θ_{NO} and θ_N the unstable branches of solutions are not visible because they almost coincide with stable branches.

Bistability can be found only at relatively low temperatures. For example, Fig. 1 does not show multiple steady states because the temperature is quite high (650 K). At lower temperatures, bistability can also be discovered when S_{cat} is varied. However, in this study we are not interested in the multiplicity of steady-states. Our primary goal is to describe the effect of non-monotonic dependence of the NO conversion on the catalyst surface area. This effect is more pronounced at higher temperatures when the rate of the NO formation becomes essential but bistability is not observed.

The plots of the steady-state NO conversions against temperature for several values of S_{cat} are presented in Fig. 5. Here, only the stable branches are shown. These results correspond to an experimental setup in which the steady-states conversions are measured using gradual increase of temperature in small steps. Qualitatively similar results were measured on Pt/Al₂O₃ catalysts for different Pt loadings [6] (with C₃H₆ as a reducing agent). In Fig. 5 one can see that as S_{cat} decreases, the peak activity moves to higher temperature and the maximum NO conversion decreases. It should be noted that the same curves can also be calculated by variation of the flow rate for the fixed values of S_{cat} , but in this case the peak activity moves to higher temperature when F increases. One can notice that, for example, at $T = 800$ K the catalyst with very low surface area ($S_{cat} = 10^{-6}$ m²) gives ~12.2% of NO conversion, but only ~37.4% of CO conversion. At the same time, the catalyst with very

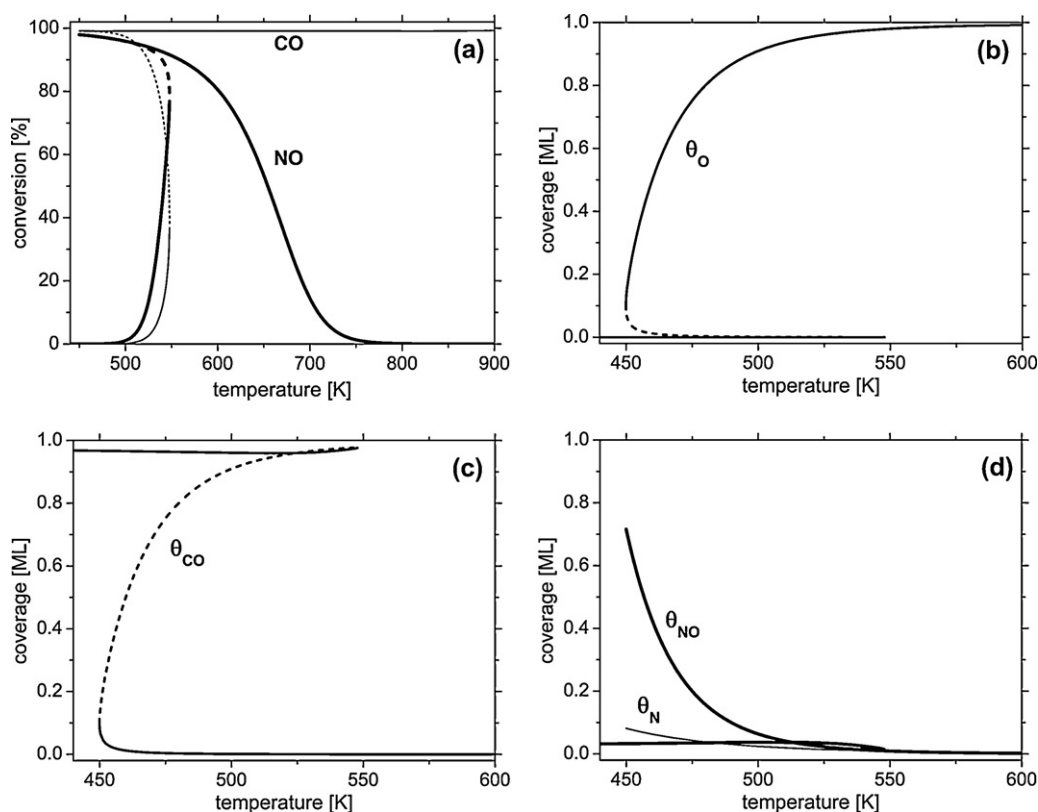


Fig. 4. Effect of temperature on the steady-state solutions at $S_{cat} = 0.01$ m². (a) CO and NO conversions; (b) adsorbed CO coverage; (c) adsorbed O coverage; (d) adsorbed NO and N coverage. Solid lines denote stable solutions while dashed lines denote the unstable ones.

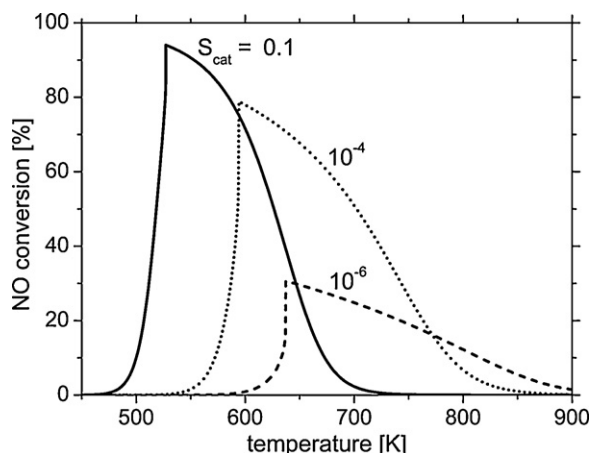


Fig. 5. Conversion of NO to N_2 with increasing temperature for three different values of $S_{cat} = 0.1, 10^{-4}, 10^{-6}$ [m²].

high surface area ($S_{cat} = 0.1$ m²) gives only ~0.018% of NO conversion, but ~99.74% of CO conversion. Thus, at high temperatures, the catalyst with very low surface area is much more active with respect to NO reduction, but it is insufficiently active with respect to CO reduction. These findings raise a question of how to construct a reactor which could remove both NO and CO efficiently (e.g., due to inhomogeneous distribution of catalyst along a reactor, transient flow reactor, multi-chamber reactor, etc.).

In most cases, an increase of active catalyst surface area should give better conversion of reactants to products. We showed, however, that this is not certainly the case for the catalytic removal of NO by CO in the presence of excess oxygen. For this reaction system, the conversion of NO to N_2 can be reduced when the catalyst's surface area increases. When the surface area is too large, a significant amount of CO is consumed, so that P_{CO} is very low inside the CSTR, and the catalyst surface becomes inhibited by adsorbed oxygen. As a result, the rate of NO formation becomes almost equal to the rate of NO dissociation, and NO-to- N_2 conversion tends to zero. That "unusual" effect is observed only at sufficiently high temperatures when the reaction of NO formation becomes essential. Increase of catalyst surface area can be detrimental with respect to NO conversion because the amount of the reductant (CO) becomes insufficient to attain the effective removal of NO.

4. Conclusions

Total cost of heterogeneous catalytic systems is mainly determined by the amount of the expensive noble metals. This problem has been traditionally addressed by search for less expensive but efficient catalysts. The model considered in this work demonstrates

that in some cases a decrease of noble metal loading in the catalytic reactor not only lowers its cost, but also may improve its efficiency. Another paradox, which follows from our results, is that an addition to a catalyst of an inert material, which blocks the active catalytic sites, can be interpreted in an opposite way – an inert material, or even an inhibitor, seemingly behaves like a promoter. Of course, these paradoxes are relevant only to a particular reaction – catalytic removal of NO by CO (or hydrocarbons) in the presence of excess oxygen. On the other hand, similar examples for other complex reactions could probably also be discovered. Therefore, our results could be interesting from a fundamental point of view, even if experimental data do not match with the model. In our case, there are numerous experimental data which strongly support the predictions of the model.

Understanding the fundamental chemistry of catalytic reactions is crucial in developing the most efficient materials. At present, the NSR, SCR and direct decomposition of NO are still the challenging tasks in catalysis research; these important problems can hardly be solved without deep understanding of the basic features of the NO decomposition reactions. We hope that our study can contribute to the fundamental theory of heterogeneous catalysis, and also to better understanding of the various experimental data concerning NO removal in the presence of excess oxygen. In addition, it can be helpful in the generation of ideas for the synthesis of novel catalysts. In this work, we considered only the simplest CSTR model. The results for more realistic dispersed plug flow model will be considered in a separate publication.

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